FWP Summaries

Materials Science Division
Argonne National Laboratory

November 2005

B&R Code	FWP	Title
KC020101	58405	Electron Microscopy Center for Materials Research
KC020103	58307	Interfacial Materials
KC020103	58930	*In Situ* Alloy Oxidation
KC020201	58701	Neutron and X-ray Scattering
KC020201	58926	Synchrotron Radiation Studies
KC020202	58806	Dynamics of Granular Materials
KC020202	58823	Mesoscopic Superconductivity
KC020202	58906	Superconductivity and Magnetism
KC020202	58916	Emerging Materials
KC020202	58918	Magnetic Films
KC020203	59001	Condensed Matter Theory
KC020203	59002	Materials Theory Institute
KC020203	59003	Quantum Computation with Electron Spins
KC020301	57504	Nanostructured Thin Films
KC020301	57525	Nanostructured Biocomposite Materials for Energy Transduction
KC020301	58510	Molecular Materials
KC020301	58600	Directed Energy Interactions with Surfaces
KC020301	58601	Fundamental Studies of Electrocatalysis for Low Temperature Fuel Cell Cathodes

Laboratory Name: Argonne National Laboratory
B&R Code: KC020101

FWP and possible subtask under FWP:
Electron Microscopy Center for Materials Research

FWP Number: 58405 (including FWP 58406 through Sept. 2004)

Program Scope:
The focus of this program is to conduct and enable materials research using advanced microstructural characterization methods based on electron beams with emphasis on the role of microstructure and defect structure on materials behavior. A strong focus is the *in situ* observation of the dynamics of processes. The EMC maintains unique resources and facilities for basic scientific research, and develops new capabilities in instrumentation, techniques, and scientific expertise.

Major Program Achievements (over duration of support):
We have developed several new methods for quantitative imaging and diffraction:
- We have made an advance in image simulation under weak diffraction contrast conditions and in diffuse scattering from defects that allow the physical structure of defects to be measured. Knowing the defect structure provides new information on their role on physical, electrical, or magnetic behavior and offers new pathways to control them.
- We have used fluctuation electron microscopy to provide new insight into the medium range order of amorphous materials, demonstrating the crucial link between medium-range order in metallic glasses and subsequent quasicrystal formation during devitrification of the glass, a long-held hypothesis unproven until now.

We have made significant advances for *in situ* capabilities through new hardware development and new concepts:
- A novel sample stage for dynamic magnetic experiments inside a TEM has been built, and we have characterized the magnetization behavior of magnetic arrays and single particles. Using Lorentz TEM and STEM, we measured the vortex state in Permalloy disks and demonstrated that this can be used to determine the chirality of lithographically fabricated patterned arrays. This information is leading to new understanding of the interactions between magnetic particles.
- As part of the Transmission Electron Aberration-corrected Microscope (TEAM) project, we have developed new designs for optics that will provide powerful new opportunities for imaging in aberration corrected microscopes. Specifically, these designs offer the possibility of atomic scale chemical imaging using energy filtered imaging and spectroscopy.

We have established several new techniques for analysis of materials:
- We have developed scanning confocal electron microscopy (SCEM) for imaging buried structures in thick specimens with resolution equal to or better than typical X-ray microscopes, yet able to perform such measurements as much as 100 times faster, using conventional laboratory space, and operated by a single trained researcher.

Program Impact:
The techniques and methodology developed within this program directly facilitate the ability of EMC users and collaborators to perform state-of-the-art measurements in next generation nanostructures. New design concepts for aberration-correcting optics are a crucial aspect of the TEAM project and future aberration correction development. Developments in analytical spectroscopy, quantitative TEM and fluctuation microscopy, and *in situ* experiments are well recognized.

Interactions:
As a national user facility, the EMC now interacts with more than 150 users per year, with 282 users and co-proposers in FY05. Strong research collaborations include: government research institutions (ORNL, Ames, LANL, SNL, NASA); universities (UIUC, NWU, NIU, UND, Cincinnatti, Pitt.); foreign institutions (Oxford, Cambridge, ANSTO, Univ. of Melbourne, ORNL, NIST, NASA, UIC, Cornell Univ. INFM-National Center); and industry (L'Oreal Researche, Radiant Detectors, FEI, JEOL, American Superconductor Corp., SuperPower).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Over 40 invited presentations at major conferences and workshops during this period. 2003: US Patent #6548810: The Scanning Confocal Electron Microscope, 2003 R&D 100 Award (Zaluzec), 2004 - August Kohler Award (Zaluzec), 2005- University of Illinois College of Engineering Distinguished Alumni Award (Zaluzec).

Personnel Commitments for FY2005 to Nearest +/- 10%:
B. Kabius (100%), M.A. Kirk (100%), D.J. Miller (50%), N.J. Zaluzec (100%); R. E. Cook (100%), J. Hiller (100%), R. Birtcher (33%); Z. Liu (PD, 100%), R. Arenal de la Concha (PD, 50%), A. Liu (PD, 50%)

Authorized Budget (BA) for FY03, FY04, FY05:

FWP 58405	**FY03: BA** \$2,302K	**FY04: BA** \$2,393K	**FY05: BA** \$2,201K
FWP 58406	**FY03: BA** \$191K	**FY04:** combined with FWP 58405	

Laboratory Name: Argonne National Laboratory
B&R Code: KC020103

FWP and possible subtask under FWP:
Interfacial Materials

FWP Number: 58307 (including FWP 58305 through Sept. 2005)

Program Scope: This program combines advanced materials synthesis, complementary *in situ* and *ex situ* characterization and property measurement techniques with computer simulations to elucidate how interfacial structure and composition control the functional properties of nanoscale oxide thin film heterostructures. The ability to manipulate the film microstructure, from single crystalline to random or columnar coarse-grained to nanocrystalline and amorphous, represents a unique feature of the program. The complementary strengths of simulation and experiment provide fundamental insights into the mechanisms and interfacial driving forces that control composition and microstructure and thus overall film properties. An increased research emphasis will be on *in situ* studies of domain dynamics in ferroelectric and ferromagnetic materials, and on studies of bio-ferroelectric interfaces, to correlate with microstructure/chemistry. Computer simulation will remain a strong component of the program through a new appointment to replace Dieter Wolf.

Major Program Achievements (over duration of support):
In-situ studies of complex oxides: Using a unique integrated MOCVD film growth, x-ray scattering and fluorescence facility at the Advanced Photon Source, we have determined ferroelectric domain wall structure and energetics for the first time in thin films. We have demonstrated the existence of ferroelectricity in epitaxial three unit cell thick $PbTiO_3$ (PTO) films, revealing the thinnest perovskite ferroelectric film that exhibits spontaneous polarization.
Atomistic simulation of ferroelectric perovskites: The first interatomic potentials capturing ferroelectricity in perovskites, including the full phase diagram, have been developed and used to study solid solutions and heterostructures.
Multiscale simulation of polycrystalline materials: A novel multiscale computational approach that incorporates all relevant length and time scales has been developed, enabling prediction of the thermomechanical behavior in polycrystalline materials. This effort is closely connected with the BES Computational Materials Science Network.
Studies of complex oxide phenomena at the nanoscale*:* *In situ* nanoscale studies of growth and interface processes in novel high-K dielectric amorphous/silicon heterostructures revealed new room temperature oxidation thermodynamics/kinetics in complex oxide layers. We developed top-down (e-beam lithography) and bottom-up approaches to produce ferroelectric nanostructures and used *in situ* and *ex situ* characterization techniques to reveal previously unobserved 90˚ domain switching dynamics in nanostructures due to released substrate constrains.
Thermal transport in solids and liquids: Significant improvements in control of thermal transport in nanostructured solids and fluids have been obtained through experimental and simulation investigations. For liquids containing small quantities of dispersed nanoparticles, controlling the degree of particle-particle interactions via control of surface charge is the key to obtaining maximum enhanced thermal conductivity. For ultrananocrystalline diamond (uncd) films the interfacial thermal resistance controls the film thermal conductivity. Although uncd has much larger interfacial conductivity than any previously studied material, the resulting net thermal conductivity is still small.

Program Impact: By combining advanced experimental tools and simulation, we have developed an unprecedented understanding of the impact of specific defects (grain boundaries, nonstoichiometry, interfaces) on material behavior. We have established metal-organic chemical vapor deposition as a premier method for the fabrication of high-quality complex oxide films that are recognized as standards against which other films are judged.

Interactions: Internal: Synchrotron Radiation Science (ANL58926), Electron Microscopy Center (ANL58405), Alloy Oxidation (ANL58930), Molecular Control of Synthesis (ANL57504), Advanced Photon Source, Energy Technology Division; External: 16 universities in the US, universities in Argentina, Germany, UK,; LBL, industry including INTEL, TI, and Structured Materials Industries. Lead laboratory for CESP Project "Nanoscale Phenomena in Perovskite Thin Films", including ORNL, SNL, and LLNL.

Recognitions, Honors and Awards (fully or partially supported by this FWP or subtask): Wolf: DOE Basic Energy Sciences Award for Sustained Outstanding Research in Metallurgy and Ceramics, Fellowship of American Physical Society, Max-Planck Research Award; Auciello: 2003 Hispanic Engineering Award, 2003 R&D 100 Award, more than 100 invited talks between FY2003 and FY2006; Petford-Long: 2005 Election to Fellowship of the Royal Academy of Engineering.

Personnel Commitments for FY2005 to Nearest +/-10%:
A Petford-Long (Group Leader: 100% from Aug 05) O Auciello (100%), G Bai (100%), J Eastman (30%), S. Streiffer (50%), L Thompson (80%), D Wolf (70% to Mar 06), R Ding (Postdoc, 50%), P Baldo (50%), J Li (postdoc, 100%).

Authorized Budget (BA) for FY03, FY04, FY05:

FWP58307:	**FY03 BA $**1,735K	**FY04 BA $**1,695K	**FY05 BA** $1,925K
FWP58305:	**FY03 BA** $190K	**FY04 BA** $195K	**FY05** joined to FWP 58307

Laboratory Name: Argonne National Laboratory
B&R Code: KC020103

FWP and possible subtask under FWP:
In Situ Alloy Oxidation

FWP Number: 58930 (including 58403 through Sept. 2004)

Program Scope: This program is developing a mechanistic understanding of the atomic-level and mesoscopic processes associated with oxidation and reduction behavior at surfaces and interfaces. A major emphasis is placed on understanding the earliest stages of metal and alloy oxidation, the initial steps of adsorption of oxygen on a clean surface and nucleation of oxide nano-islands, that set the stage for the ensuing formation of a continuous, macroscopically-thick oxide layer. The program focuses on the relationships between early-stage oxidation behavior and subsequent growth, strain development, and creep behavior of continuous, macroscopically-thick oxide layers, emphasizing the fundamental mechanisms of protective oxide formation. The effects of supported nano-island structure and chemistry on the catalysis of important energy-related redox reactions are an additional major focus. Our approach uses a unique combination of in-situ synchrotron x-ray and electron microscopy techniques providing structural, chemical, kinetic, and thermodynamic information in controlled, oxidizing environments.

Major Program Achievements (over duration of support):
Alloy-oxide phase equilibria: Using in-situ x-ray scattering techniques that we developed at the Advanced Photon Source (APS), we discovered that the pO_2 for equilibrium between Cu_2O nano-islands and Cu differs dramatically from predictions of bulk thermodynamics. This observation has a number of important implications, *e.g.*, for controlling the behavior of supported oxide nano-islands as heterogeneous catalysts of redox reactions.
Compositional effects on oxide island coalescence: Using in-situ transmission electron microscopy, we discovered that alloying Cu with Au leads to substantially slower oxidation kinetics and the formation of oxide islands with dendritic morphology. This observation is providing new insight into the factors that control the formation of continuous, protective oxides on alloy surfaces.
Strain development and deformation behavior during continued oxidation: We modified the Debye-Scherrer technique to measure growth strains in-situ at the APS with unprecedented accuracy and precision (precision of 10^{-5} in strain). Such in-situ measurements are critical to providing insight into the key processes controlling formation and lifetime of protective oxides.
Reactive element effect: In-situ x-ray experiments determined that the presence of a dilute quantity of Zr or Hf added to β-NiAl changes the stress state of the oxide that forms on the alloy at high temperature from compressive to tensile, leading to dramatic improvement in the performance of the protective oxide.
Strain generation mechanisms in thermally grown protective aluminas: Large strains caused by phase transitions, composition change, internal growth, thermal expansion mismatch (and strain relaxation with creep processes) have been identified and quantified through this program's pioneering in-situ x-ray studies. The unique ability that in-situ techniques provide in separating different strain contributions is essential for understanding oxide development and failure mechanisms.

Program Impact: The program provides fundamental insight into improving the behavior of high temperature protective oxide coatings, and fundamental understanding relevant to the growing number of applications that depend on controlled oxidation to form stable, thin oxide layers (*e.g.,* MRAM, gate-oxide layers, and gas sensors). Our experiments illuminate the roles of structure and chemistry on the activity and lifetime of supported catalysts for energy-related redox reactions.

Interactions: Internal: Interfacial Materials (ANL58307), Synchrotron Radiation Science (ANL58926), Electron Microscopy Center (ANL58405), Advanced Photon Source; External: Lawrence Berkeley National Laboratory, Oak Ridge National Laboratory, Case-Western Reserve University, University of Pittsburgh, University of Illinois-Urbana Champaign, University of Florida, MPI Stuttgart (Germany).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask): B. W. Veal and A. P. Paulikas: Listed in Science Watch (vol. 8, p. 1, 1997) among 30 most cited scientists in the physical sciences (1990-1996). B. W. Veal: ANL Exceptional Performance Program, 1992 and 1996.

Personnel Commitments for FY2005 to Nearest +/- 10%: P. Baldo (50%), R.C. Birtcher (70%), J.A. Eastman (Group Leader, 70%), A.P. Paulikas (100%), L.E. Rehn (60%), L.J. Thompson (20%), B.W. Veal (90%), D. Wolf (30%), G.-W. Zhou (Postdoc, 100%).

Authorized Budget (BA) for FY03, FY04, FY05:

FWP 58930	**FY03 BA** $698K	**FY04 BA** $1,396K	**FY05 BA** $1,340K
FWP 58403	**FY03 BA** $698K	**FY04** joined to FWP 58930	

Laboratory Name: Argonne National Laboratory
B&R Code: KC020201

FWP and possible subtask under FWP:
Neutron and X-ray Scattering

FWP Number: 58701

Program Scope:
Members of the neutron and x-ray scattering group enable the Division to pursue strong multidisciplinary research programs that are possible only with state-of-the-art scattering capabilities combined with creative synthesis of new materials, theory, and other experimental tools. Priority is given to research topics that anticipate the full capability of the Spallation Neutron Source. World-wide neutron and x-ray scattering facilities are used. One group member also operates a research instrument at the IPNS, serving a broad user community. An important goal of the group is to strengthen the neutron user community in the US in preparation for the SNS. Sponsoring an annual summer school on neutron and X-ray scattering is a key part of this activity. Group members also participate in conception, design, and review of instrumentation for the SNS. More detail is available at http://www.msd.anl.gov/groups/nxrs/index.html.

Major Program Achievements (over duration of support):
Superconductors: World class research on the relationship of chemical composition and crystal structure to the properties of superconducting materials has extended for many years, and has most recently focused on the newly discovered compound $Na_xCoO_2 \cdot 4xH_2O$. A new program focuses on the high-pressure synthesis of new layered superconducting materials and their characterization by neutron powder diffraction.
Orbital Correlations, Frustration, and Self-Organization: A comprehensive research program in layered manganites has provided the most detailed models of Jahn-Teller polaron correlations competing with ferromagnetic order in any CMR compound. Using techniques such as inelastic neutron scattering and diffuse x-ray scattering, we have obtained new insights into spin-state transitions in cobaltites and orbital dimerization in layered ruthenates.
Magnetic Behavior in Constrained Geometries: Argonne scientists pioneered neutron reflectometry and have applied it to critical problems in polymer science and the magnetism of thin films and multilayers. Applications include studies of long-standing problems such as exchange coupled superlattices and exchange bias in thin films. We have started a new program studying the effect of annealing on the magnetic coupling of exchange bias systems used in spin valves.
SNS Instrument Concepts: A prototype spin-echo-resolved grazing-incidence scattering instrument at the ILL yielded results that confirm the viability of this new method for the study of biological and polymeric membranes. A full SNS instrument and a new research program in this area are being pursued. Instrumentation for diffuse neutron scattering with elastic discrimination is being prototyped at the IPNS in preparation for full instrument designs for the SNS. These instruments will open new areas of science to neutron scattering.

Program Impact:
Work of the group in many different science areas is recognized world wide as leading the field and opening new research directions. Close interaction with new-materials synthesis, other experimental work, and theory is a widely-recognized strength of the group. The impact of research done by the group is evidenced by 68 archival publications, with 464 citations, and 64 invited talks at major meetings during 2002-2005.

Interactions:
Group members collaborate with most other groups in the Division and with a large number of scientists at universities and other national laboratories, as evidenced by over 150 coauthors on papers published 2002-2005.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
J. Jorgensen: B. E. Warren Diffraction Physics Award (1991), C. E. Barrett Award in Powder Diffraction (1997), Among 100 most highly cited physicists (ISIhighlycited.com). G. P. Felcher: Humbolt Award, 1999.

Personnel Commitments for FY2005 to Nearest +/-10%:
J. D. Jorgensen (Group Leader) (100%), G. P. Felcher (100%), R. Osborn (100%), S. Rosenkranz (100%), S. Short (100%), S. G. E. te Velthuis (100%)

Authorized Budget (BA) for FY03, FY04, FY05:
FY03: BA $2174K **FY04: BA $**2169K **FY05: BA $**2613K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020201

FWP and possible subtask under FWP:
Synchrotron Radiation Studies

FWP Number: 58926

Program Scope:
This program develops new capabilities using the nation's synchrotron radiation facilities and applies them to key problems in materials science. In particular, we aim to play a leading scientific role at the Advanced Photon Source (APS). X-ray scattering studies take advantage of the high brilliance APS x-ray source for in-situ studies of synthesis and structure of ultrathin films of complex oxides, and interfaces in electrochemical and catalytic systems. High-resolution angle-resolved photoemission is used to understand the nature of superconductivity in the High-T_c materials. Other thrusts focus on exploring science enabled by future facilities such as an x-ray nanoprobe, a high-energy photoemission facility, and a coherent, femtosecond x-ray source.

Major Program Achievements (over duration of support):
Vapor-Phase Epitaxy: We have used in situ x-ray scattering to understand the atomic-scale growth mechanisms and surface structures occurring during MOCVD growth of GaN and $PbTiO_3$. Homoepitaxial growth mode transitions and surface reconstructions were mapped as a function of process conditions for the first time.
Quasiparticles in High-T_c Superconductors: The nature of the carriers in high-T_c superconductors has been elucidated using angle-resolved photoemission. We have identified a particular point on the Fermi surface where the superconducting energy gap vanishes below T_c, and determined the nature of the excitations that dominate the properties of the system.
Nanoscale Ferroelectricity: The minimum system size needed to support ferroelectricity has long been a subject of debate. We have recently demonstrated ferroelectricity in the most confined perovskite system yet, namely $PbTiO_3$ films as thin as three unit cells.
X-ray studies of catalyst under near atmospheric gas pressure: Adsorption of CO is one of the most important issues in catalysis because of its poisoning of catalytic activity. Using innovative in situ x-ray techniques, we established the long-range-ordered nature of the CO overlayer on the Pt(111) surface under (near) atmospheric pressure of CO gas. A previously unobserved high-density structure was discovered, and a temperature-pressure phase diagram including the CO desorption boundary was determined.
Time-Correlation Spectroscopy with Coherent X-rays*:* We have developed this new technique for observing atomic- and nano-scale dynamics and used it to observe non-linear diffusion in concentrated colloids and fluctuations during domain coarsening. These studies with coherent x-rays are providing part of the scientific basis for the next generation of synchrotron x-ray sources.

Program Impact:
The Synchrotron Radiation Studies group publishes an average of 30 refereed articles every year, typically including 4 articles per year in Physical Review Letters, Science, or Nature. These articles are highly cited; based on citation rate, our average paper is in the top 1% of papers in materials science.

Interactions:
This project provides expertise in synchrotron techniques to collaborations with several Materials Science Div. groups (esp. FWP 59001, 58307, 58930 and 58601), other ANL Divisions (esp. Experimental Facilities), and with researchers at more than 30 universities, academic institutions, and industrial laboratories worldwide.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
J. C. Campuzano was appointed Scientific Director of Univ. of Wisconsin's Synchrotron Radiation Center in 2002. Each year about two dozen invited talks are given by group members.

Personnel Commitments for FY2005 to Nearest +/- 10%:
Staff: J. C. Campuzano (50%), P. H. Fuoss (100%), N. Markovic (10%), H. You (50%), G.B. Stephenson (40%); Term Staff: D. Fong (100%); Visiting Faculty: M. Bedzyk (10%); Postdocs: F. Jiang (50%), A. Menzel (100%).

Authorized Budget (BA) for FY03, FY04, FY05:
FY03: BA $857K **FY04: BA** $1,340K **FY05: BA** $1,800K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020202

FWP and possible subtask under FWP:
Dynamics of Granular Materials

FWP Number: 58806

Program Scope:
This program focuses on theoretical and experimental analysis of the physics of granular materials. We consider the experiments, the theory, and large-scale molecular dynamics simulations of partially fluidized granular flows in application to granular avalanches, gas-fluidized beds, and dynamic self-assembly of microparticles in weakly conducting liquids subject to electromagnetic field. New research directions were recently extended towards biological objects – self-organization and control of active bioparticles in confined geometries.

Major Program Achievements (over duration of support):
• Dynamics of thin layers of granular materials subject to controlled airflow modulation: We discovered a novel method to fluidize small and cohesive grains with a high degree of homogeneity. The secret lies in the use of modulated gas flow to drive the fluidization. We find a remarkable improvement in the quality of the fluidization, where parasitic gas channels are virtually eliminated. Furthermore, we developed a high-speed fluorescent video microscopy method to characterize the parameters of the fluidization. Our studies reveal that the dramatic increase in fluidization efficiency comes from the enhancement of particle diffusion as a result of the onset of disordered subharmonic patterns. • Self-assembly and pattern formation in magnetically driven granular systems at liquid surface: We developed a new method based on ac magnetic field modulation to orchestrate the self-assembly of an ensemble of magnetic microparticles suspended on a liquid surface. With this method, we created a novel snake-like magnetic structure out of 40-90 micron sized magnetic particles. While each segment of the 'snake' is composed of ferromagnetically aligned chains of microparticles, neighboring chains assemble antiferromagnetically hence displaying a remarkable hierarchical co-existence of different magnetic states. Our research demonstrates that these astounding self-assembled structures are due to surface waves in the liquid generated by the collective response of magnetic microparticles to an alternating magnetic field. • Self-organization and control of active bioparticles: We initiated a new research direction which applies the theoretical and experimental aspects of dynamic self-assembly found in granular matter to the self-organization of active bio-organisms such as Bacillus subtilis, a rod-shaped bacteria, capable of swimming up to 20 microns/second. The hydrodynamic and chemical interactions between individual cells results in a remarkably rich collective behavior ranging from self-concentration of bacteria due to gradients of dissolved oxygen or pH level to phase transitions and self-organization in confined geometries. The self-organization takes the form of coherent structures with sizes that are many times larger than those of the individual bacteria. We investigated the emergent collective behavior in dense bacterial colonies confined in a thin liquid film of controlled thickness. We devised a method of controlling the density of the bacteria colony by transmitting electric current, enabling studies of the scale of the emergent dynamic structures as a function of cell concentration. We developed a continuum mathematical model of this phenomenon to demonstrate that the primary mechanism of self-organization is associated with the shear flow induced deflection of bacteria orientation.

Program Impact:
Our phenomenological approach to non-equilibrium behavior, in general, and granular materials in particular, established it as a legitimate theoretical tool for the worldwide scientific community. • Our newly developed experimental approach on controlled airflow modulation of granular matter provides a new avenue to achieve uniform fluidization of granular material which could greatly benefit the petroleum and pharmaceutical industries where efficient control and uniform mixing of micro-catalysts remain a problem. • The manipulation of magnetic micro-particles provides a new means to create networks of conducting wires through self-assembly. • Control of bio-objects by dynamic self-assembly constitutes a new approach which can be applied to the emerging bio-chip and biofilm technology.

Interactions:
UC San Diego; U. of Kansas; LANL; Northwestern U.; Hebrew U. of Jerusalem, Israel; CEA Saclay, Fr.; ESPCI, Paris, France; Inst. of Theor. & Expt. Physics, Moscow, Russia; U. of Arizona.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask): 6 high-profile papers in FY05: 3 Phys Rev Lett., 1 Europhys. Lett.; 2 featured stories in popular science magazines; 1 review in Rev. Mod. Phys. was placed in the top 1% within its field in 2004. Organized 1 Intl. School, delivered invited lecture series, 5 invited talks.

Personnel Commitments for FY2005 to Nearest +/-10%: I. Aronson (100%), W. Kwok (30%), A. Snezhko (100%), Andrey Sokolov (100%), D. Rosenmann (20%).

Authorized Budget (BA): **FY03:** BA $591K **FY04:** BA $580K **FY05:** BA $500K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020202

FWP and/or subtask Title under FWP:
Superconductivity and Magnetism

FWP Number: 58906 (includes 58823 through Sept. 2004)

Program Scope: This program makes in-depth experimental and theoretical investigations of fundamental phenomena in novel superconducting and hybrid materials at all length scales. Using nanotechnology tools for physics, we engineer novel structures whose small dimensions and electronic tunability facilitate the exploration of new phenomena and devices arising from confinement, proximity, and collective effects which could dramatically alter the physical properties and response to external fields and currents. We maintain leading programs in synthesis, experiment and theory, deriving strong benefit from their synergy.

Major Program Achievements (over duration of support):
Novel nanostructured superconductors: •We developed a new fabrication route for superconducting nanostructures by combining the purity of single crystal $NbSe_2$ with focused-ion-beam nano-patterning and metal evaporation. These crystal-heterostructures have atomically flat surfaces and clean metal/superconductor interfaces and enable STM studies of vortex confinement and proximity effects such as FFLO state and π-junctions at an unprecedented atomic scale. We successfully imaged vortices in their confined state with STM and discovered a series of vortex structural transformations •We developed a novel procedure based on metal vapor transport to produce nanowires of $NbSe_2$with unprecedented long lengths and immune to surface impurities and oxidation. They provide a new stage for quantum transport measurements to explore quantum and thermal phase slip phenomena. •We pioneered new electrochemical deposition techniques for synthesizing superconducting Pb 3D mesocrystals with self-assembled geometries. These crystals exhibit novel confinement behavior, transforming from a type I to type II superconductor with decreasing temperature. Simulations based on 3D Ginzburg-Landau formalism predict the co-existence of giant and multi-quanta vortex states.
New superconducting materials: •We synthesized the newly discovered 11.5K graphite intercalated superconductor CaC_6 whose electronic structure bears a striking resemblance to that of the multi-band 40K superconductor, MgB_2. We mapped out its superconducting anisotropy with micro-calorimetry and found a rather low anisotropy of $\Gamma \approx 3.7$, highlighting the importance of the metal-derived s-band in the formation of superconductivity. •We measured the quasiparticle density of states in off-axis MgB_2 epitaxial films with STM to study the applicability of two-band superconductors for planar junctions/electrodes and revealed current losses arising from surface misaligned crystalline MgB_2 facets which are undetected by x-rays.
Vortex physics: • Our theoretical description of crossing Josephson and pancake vortex lattices and their dynamic behavior is acknowledged world-wide in quantitatively explaining new vortex phases such as the chain states found in highly anisotropic BSCCO superconductor and in developing new schemes to control the viscosity of moving Josephson vortices with magnetic field. •Combining Josephson plasmon oscillations with photonic principles, we developed a new principal means to extract surface terahertz emission from meso-scale BSCCO mesas with metallic Bragg gratings (patent disclosure).
Emerging areas: • New work on nanophotonics demonstrated semi-circularly arranged nanoholes in thin metal films act as point sources of surface plasmons which can be focused into a high intensity, sub-wavelength spot. The electric field in this spot is strong enough to induce non-linear optical phenomena needed for photonic logic and for enhanced optical spectroscopy of adsorbed molecules. • H_2 research-developed patentable ultra-fast response H_2 sensors based on nano-granular Pd films.
Program Impact: Edited Physica C special edition on MgB_2 (2003); Physics Today cover page on MgB_2 (2003); Meso-crystal work in Science Editors' Choice highlight (2004); Surface plasmon work featured in Laser Focus World (2005); H_2 nanosensors featured in Nanotechnology Now and Science Daily.
Interactions: Our collaborations extend within MSD, CHM, BIO, MTI, CMT, APS and worldwide.
Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask): 2003 Kamerlingh-Onnes (Crabtree) and John Bardeen (Vinokur) Prizes; Editorship Physica C (W. K. Kwok); NHMFL program/user committee (U. Welp); Patents related to Magneto-optic Current Sensor (#6,630,819) and Superconducting MEMS (# 6,638,895);
Personnel Commitments for FY2005 to Nearest +/- 10%: W. K. Kwok (40%) G. Karapetrov (75%). E. Koshelev (25%) M.Iavarone (50%) Vlasko-Vlasov (20%) M Vinokur (20%) U. Welp (60%) D. Rosenmann (50%) Zhili Xiao (20%) Andreas Rydh (50%)
Authorized Budget (BA):

FWP 58823	**FY03: BA $278K**	**FY04: combined with 58906**	
FWP 58906	**FY03: BA $906K**	**FY04: BA $1,010K**	**FY05: BA $940K**

Laboratory Name: Argonne National Laboratory
B&R Code: KC020202

FWP and/or subtask under FWP:
Emerging Materials

FWP Number: 58916 (including FWP 58802 through Sept. 2004)

Program Scope: The Emerging Materials effort explores the fundamental science of complex materials exhibiting collective electronic, magnetic and structural behavior. Materials synthesis is integrated with properties measurement to reflect our philosophy that these should be synergistic: new materials expose novel phenomena and call for innovative measurements, while a deep fundamental understanding demands new or higher quality materials. We emphasize low-dimensional systems via tailored crystal structures. Present and future research concentrates on metal-insulator transitions (MIT), phase competition and short-range order, new geometrically frustrated magnets and quantum critical materials. We include exploratory and strategic synthesis, where the latter is a targeted approach to extract the science in known materials. We grow crystals using zone, flux and vapor transport methods and by high-pressure synthesis. Property measurements discover and illuminate key issues focusing on electronic and magnetic interactions, and importantly provide immediate feedback to the materials grower that propels forward the synthesis program. Thus while all our research is enabled by our high-quality samples, the relationship is reciprocal. We specialize in tunneling and transport measurements that are augmented by collaborations at the APS on x-ray magnetic dichroism, inelastic scattering and diffraction, at the IPNS on magnetic and physical structure and at the EMC on electron scattering. Together these help elucidate the mechanisms underpinning, e.g., high-T_C superconductivity, the MIT and the delicate balance between short- and long-range order in manganites.

Major Program Achievements (over duration of support): We discovered from x-ray dichroism and tunneling that the outermost Mn-O bilayer of bilayer manganites, alone, is an intrinsic insulating nanoskin with no long-range ferromagnetic order while the next bilayer is metallic with the full bulk spin polarization up to T_C. The result plus ARPES data from two collaborators (Shen, et al and Dessau, et al), establish our crystals as the ‘gold’ standard for manganite surface studies. Our growth of $La_{1-x}Sr_xCoO_3$ crystals has enabled inelastic neutron scattering studies that suggest a model of dynamic orbital ordered clusters leading to competition between ferro- and antiferromagnetic coupling.
High-pressure synthesis has delivered new materials for exploration of magnetic exchange. They are heretofore unknown double perovskites $CaCu_3Fe_2M_2O_{12}$ (M=Ta,Nb,Ru) and higher Cr substitution in $SrRu_{1-x}Cr_xO_3$. Novel vapor synthesis of nanowires of TaS_3 represents the first clear example of the charge-density wave (CDW) transition in a self-assembled nanowire. Our synthesis method is general to transition metal chalcogenides, and we have used it to explore the effect of confinement on the CDW state of $NbSe_3$ and to generate superconductors of $NbSe_2$ and TaS_2. Our rapid response in the synthesis of MgB_2 enabled our tunneling data to first identify self-energy effects due to interband quasiparticle scattering and also the absence of additional interband scattering after 10% C doping. Our seminal transport results on manganites: developed a spin-wave model for double exchange; identified metallic nature of conduction below T_C; identified first-order MIT; and solved a complex magnetic structure. Our tunneling data, on our high T_C superconductor crystals of $Bi_2Sr_2CaCu_2O_y$, together with photoemission and neutron scattering data of others, have strongly implicated spin excitations as the pairing mechanism.

Program Impact:
Our program boasts >522 publication citations (for papers published in the past three years). Our world-renown synthesis effort addresses the most exciting science and often drives the research agenda of internal and external collaborators. Our tunneling and anisotropic transport programs are at the cutting edge of research worldwide. In three years, our research has produced over 60 refereed papers with 12 in high visibility journals (PRL, Nature or Science), 22 in PRB, and >30 invited talks (3 at major international conferences).

Interactions: Internal: Intense Pulsed Neutron Source; Advanced Photon Source; and Electron Microscopy Center. External: Universities and laboratories worldwide. In the past three years, about 300 samples have been sent to over 40 unique collaborations, demonstrating the scope of outreach and impact our program delivers.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
John F. Mitchell was elected as a Fellow of the American Physical Society in 2002.
David G. Hinks has notably achieved 60 publications over his career with 60 or greater citations each.

Personnel Commitments for FY2005 to Nearest +/- 10%:
Staff: K.E. Gray (group leader) 80%, J.F. Mitchell 100%, H. Zheng 100%, D.G. Hinks (part-time staff) 40%
Postdoc: T. Wu (50%), Y.S. Hor (100%), J. Hill (50%), P. Barnes (50%), R. Macaluso (25%). Visiting Scientist: A. Bhattacharya (50%), Qing’An Li (30%), L. Ozyuzer (30%). Graduate students: D. Mazur (100%)

Authorized Budget (BA) for FY03, FY04, FY05:
FWP 58802: FY03: BA $657K **FY04: BA** $725K **FY05: combined with FWP 58916**
FWP 58916: FY03: BA $433K **FY04: BA** $645K **FY05: BA** $1,397K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020202

FWP and possible subtask under FWP:
Magnetic Films

FWP Number: 58918 (including FWP 58830 thru Sept 2005)

Program Scope:
Our goals are to create, explore and understand novel nanomagnetic materials and phenomena. Our interests include the physical, chemical and metallurgical properties of artificially layered superlattices, sandwiches, wedges, ultrathin films, surfaces, and includes lithographic patterning and self-assembly. The task is to identify fundamentally new phenomena associated with the competition between spatial and magnetic length scales and proximity effects. We want to understand the ultimate limits of miniaturization, and to work to transform the art of nanomagnet fabrication into a science. We tailor properties via preparation conditions and manipulation of dimensionality for structures grown via sputtering, molecular beam epitaxy, and novel patterning and templating strategies. We explore exchange-coupled heterostructures and those formed with superconductors, insulators and antiferromagnets. We utilize surface magneto-optic Kerr effect (SMOKE) and synchrotron probes, and operate Brillouin and Raman scattering facilities. We study basic magnetization dynamics, magneto-transport, and magneto-optic phenomena. The new phenomena that we explore extends our basic understanding of nanostructured magnetic materials and lay the foundations for emergent technologies.

Major Program Achievements (over duration of support):
Lateral Spin Valves: We patterned novel spin-injection structures and reported values of the polarization and spin diffusion length in Cu at 10 K and room temperature. Spin-polarized electrons are injected into paramagnetic Cu nanowires by driving an electric current from a ferromagnetic cobalt electrode. The non-equilibrium spin accumulation in the Cu results in a difference between the chemical potentials for spin-up and -down electrons that is detected non-locally as a field-dependent output voltage at a second cobalt electrode. The polarization is enhanced compared to previous reports, which we attribute to superior interfaces. These structures enable the separation of electric-charge and pure-spin currents, enabling the realization of entirely new spintronic concepts.

Interacting Magnetic Vortices: We trapped double magnetic vortices within micron-size elliptical corrals of permalloy and studied the spin dynamics by means of microwave resonance techniques and micromagnetic simulations. Although the ground-state energetics is independent of the relative polarizations of the two vortex cores, we were first to show both experimentally and via modeling that the dynamics of the vortex core translational modes are controlled by these relative polarizations. This serves as an elegant example of the general problem of understanding the dynamics of coupled solitons.

Spin-Polarized STM: We developed a new sample/tip heating stage that facilitated the conversion of a UHV STM to spin-polarized mode via spectroscopic imaging utilizing a magnetized iron coated W scanning tip. We demonstrated the capability by simultaneously topographically and magnetically imaging nanoscale islands of Mn on an Fe(001) whisker, and confirmed the known structure that each Mn atomic layer is magnetized in plane, but that alternate layers are aligned antiparallel to create the antiferromagnetic structure of the Mn. This opens new vistas for our studies of magnetic surfaces and nanostructures.

Program Impact:
The laterally confined nanomagnet program, started in mid-FY01, was a winner of the DOE-BES competition entitled: Complex Systems: Science of the 21st Century. We (i) help lead the theme on Electron and Magnetic Materials and Devices at Argonne's Center for Nanoscale Materials, (ii) coordinated the DOE CSP project on Nanocomposite Magnets for ten years, and (iii) provide novel samples to a broad user community at the DOE synchrotron and neutron sources and electron microscopy centers.

Interactions:
Our collaborations extend within MSD, CNM, BIO, MCS, CHM, IPNS, XFD-APS and worldwide.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
2003 UC-ANL Distinguished Performance Award (SJ); 2001 AVS Thornton Award (SB); since 2001 a group total of over 100 invited talks and 35 invited participation as co-organizer or program/advisory committee of major meetings (*i.e.* APS, AVS, ICM, ICMFS, MMM, MRS, SRMS, DOE, NSF.)

Personnel Commitments for FY2005 to Nearest +/- 10%:
S. Bader (50%), M. Grimsditch (100%), J. S. Jiang (100%), A. Hoffmann (100%), V. Novosad (100%).

Authorized Budget (BA):

FWP 58830	**FY03**: **BA** \$883K	**FY04**: **BA** \$4465K	**FY05:** combined with 58918
FWP 58918	**FY03:** **BA** \$965K	**FY04:** **BA** \$950K	**FY05:** **BA** \$1,620K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020203

FWP and possible subtask under FWP:
Condensed Matter Theory

FWP Number: 59001

Program Scope:
Condensed matter theory research programs in MSD are currently carried out in the general areas of superconductivity, spectroscopy, magnetism, and nanoscience, with emphasis on interaction with various experimental programs within MSD. More detail is available at http://www.msd.anl.gov/groups/cmt/

Major Program Achievements (over duration of support):
Superconductivity: Argued that the Migdal theorem is still valid for the electron-phonon interaction in the case of poor screening appropriate to the cuprates. Used a model of electrons interacting with gapped spin excitations to successfully describe dispersion anomalies in cuprates seen by ARPES.

Spectroscopy: Discovered the presence of strong momentum anisotropy in ARPES lineshapes in the cuprates that correlates with that of the pseudogap. Developed a new autocorrelation method for studying photoemission data as a function of transferred momentum to complement that of Fourier transformed STM. Used this analysis to argue against charge ordering in the pseudogap phase of the cuprates.

Magnetism: Predicted strong sensitivity of the Hall number with doping in the heavy fermion magnet $YbRh_2Si_2$. Used these results to suggest that this metal might be the first example of a quantum critical valence fluctuator.

Nanoscience: Predicted ferromagnetism in quantum wires due to exchange interactions in the low density limit, and connected this result to the unusual conductance plateau observed in experiment. Described spin dependent impurity scattering for Luttinger liquids in a magnetic field, and used this to suggest a novel spin filter.

Program Impact:
Work, particularly in the areas of superconductivity and mesoscopics, is recognized world-wide, with numerous invited talks given by Drs. Abrikosov, Matveev, and Norman. The collaboration on photoemission in cuprate superconductors in the past several years led to 36 papers in Nature, Physical Review Letters, and Physical Review B. Dr. Norman has 24 papers and Dr. Matveev has 12 papers with over 50 citations. Dr. Abrikosov is the author of many highly cited papers in physics, as well as two well-known books.

Interactions:
This program involves collaborations with ANL Materials Science programs on Superconductivity and Magnetism (58906), Magnetic Thin Films (58918), Synchrotron Radiation Studies (58926), Neutron and X-Ray Scattering (58701), and Emerging Materials (58916); and with programs at the University of Illinois at Chicago, Northern Illinois University, Ohio State University, Rice University, University of Minnesota, University of Washington, University of Wisconsin-Madison, IBM-Almaden, and Ames Laboratory. Also, collaborations exist with the ESPCI-Paris, SPhT-Saclay (France), RIKEN, and Hokkaido University (Japan).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Dr. Abrikosov is a member of the National Academy of Sciences and the Royal Society of London. He received the Nobel Prize in Physics in 2003. Dr. Norman received the University of Chicago Distinguished Performance Award in 1999. Both are Fellows of the American Physical Society. Dr. Matveev is a Sloan Fellow.

Personnel Commitments for FY2005 to Nearest +/- 10%:
A. Abrikosov (100%), K. Matveev (100%), M. Norman (100%), P. Sharma (100%); V. Vinokur (50%); A. Koshelev (50%); M. van Veenendaal (10%)

Authorized Budget (BA) for FY03, FY04, FY05:
FY03: BA $760,000K **FY04: BA $**1,173,000K **FY05: BA $**1,100,000K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020203

FWP and subtask Title under FWP:
Materials Theory Institute

FWP Number: 59002

Program Scope:
This program carries out forefront investigations via assembling national and international visitor research teams with complementary expertise tailored to important emerging problems in the field of materials sciences. The extensive visitor programs attract and bring together world-leading scientists for collaborative joint projects in direct support of DOE's mission. The visits can last from a few days to several months.
The program currently focuses on the physics of nanostructured materials and hybrid systems and soft condensed matter. The research projects are developed in close collaboration with MSD's experimental programs. Current research is focused along the following major themes: (1) Transport properties of arrays of quantum dots; (2) Quantum phase transitions in low-dimensional and disordered structures; (3) Quantum charge and spin transport in hybrid and disordered materials; and (4) noise and decoherence effects in nanodevices.

Major Program Achievements (over duration of support):
Theory of hopping transport in an array of metallic quantum dots**:** A new theoretical approach created under the MTI program enabled a breakthrough in understanding transport in arrays of quantum dots and resolved a 30-year puzzle regarding the mechanism of electronic transport in the insulating phase of granular metals. We demonstrated that conductivity of granular arrays is governed by hopping transport which is mediated by the process of coherent quantum cotunneling, the simultaneous quantum penetration into and coherent departure of another electron from the same grain. This assures electron hopping over several grains. The theoretical predictions were tested in experiments by the University of Chicago group and were found to be in excellent agreement with the data [PRL **95**, 076806 (2005)]. Our approach opens the opportunity for a quantitative description of transport in artificial semiconductor nanocrystals, the main building blocks for a new generation of solar cells and energy conversion units. Other theoretical achievements: theory of orbital spin-Hall effect in hopping conductors; • theory of Rabi oscillations of a qubit coupled to a two-level system; • theory of radiation from Josephson junction • theory of giant oscillations of energy levels in mesoscopic superconductors due to interplay between the Andreev and geometrical quantization; these oscillations lead to anomalous currents through quantum point contacts • theory of charge transfer between hopping insulator and superconductor: generalization of the Andreev processes – time reversal reflection mechanism was introduced • a new kind of random numbers generator marking a breakthrough in the field.

Program Impact:
Established global collaborative network: MTI – BNL – LANL – UofC – Northwestern University – University of Wisconsin – UCSD – Ruhr University – Köln University – TU Delft – Chalmers University – Oslo University – A F Ioffe Institute – CRTBT-CRNRS (Grenoble) carrying out joint projects on nanophysics and soft condensed matter physics, exchanging visits and conducting a chain of International Workshops on Nanophysics in the US and Europe. Created the program on properties of nanostructured materials which is recognized as one of the world-leading programs as evidenced by the numerous applications for participation in the Argonne Fall Workshops on Nanophysics. Advisory Committee recruited new active members to propose and design novel research topics and joint projects on the most demanding subjects, involving a wide community of researchers into DOE projects and exposing ANL achievements to the scientific community. Publications and talks during the period of September 30, 2004 – October 1, 2005: 24 publications (PRL – 9, PRB – 8, Europhys. Lett. – 4, Appl. Phys. Lett. – 1, Physica B – 1, New J. Phys. – 1) and one paper is accepted to Nature Physics, and 25 invited talks.

Interactions:
Internal: Condensed Matter Theory, Emerging Materials, Magnetic Films, Synchrotron Radiation Studies (MSD)
External (In addition to listed above): Princeton University; Syracuse University; University of Florida; Harvard; Leiden University; Helsinki Technological University; Weizmann Research Institute, Israel; Tel Aviv University, Israel; Hebrew University, Jerusalem, Israel; Coherentia-INFM, Rome, Italy; Landau Institute, Moscow; Institute for Microelectronics, Nizhny Novgorod, Russia.

Recognitions, Honors and Awards (at least in some part attributable to support this FWP or subtask):
Editorship Central European Journal of Physics [2003-present – V. Vinokur]

Personnel Commitments for FY2005 to Nearest +/- 10%:
V. Vinokur (60%), I. Aranson (20%) A. E. Koshelev (20%), I. Beloborodov (100%), A. Lopatin (100%)

Authorized Budget (BA) for FY03, FY04, FY05:
FY03: BA $281K **FY04: BA $**267K **FY05: BA $**250K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020203

FWP and possible subtask under FWP:
Quantum Computation with Electron Spins

FWP Number: 59003 (FWP funded in FY05)

Program Scope:
One of the most exciting phenomena at the nano-scale is that of quantum phase coherence and its application to quantum computing (QC). Recently, quantum computing has caught the imagination of the physics and computer sciences communities because of its powerful potential in areas of large database searches, large number factorization, and in quantum mechanical simulation of physical systems The grand challenge is to develop scalable arrays of quantum coherent nanoscale objects that would form the quantum bits (qubits) and the logic gates of a quantum computer. In this research program we develop electron spin resonance (ESR) techniques to manipulate and radio frequency-single electron spin transistor (RF-SEST) techniques to measure single electron spins in arrays of nanoscale quantum dots in order to form the scientific underpinnings of an electron spin quantum computer. The basic qubit will consist of endohedral nitrogen in C_{60}. The nitrogen spin in C_{60} has spin phase coherence times, T_2 > 20 micro-sec at room temperature. We will also make use of biological processes to attach C_{60} to DNA networks to form the array of interacting qubits, and advanced lithographic processes to form address gates and the readout tunnel junctions necessary for a quantum computer.

Major Program Achievements (over duration of support):
A key task is to prepare the qubits of endohedral nitrogen in C_{60}. N^+ ions were generated from a 3-cm Kaufman ion source and accelerated before directing them onto a C_{60} sample in a UHV chamber. Various acceleration voltages up to 575 eV and environmental parameters (ion neutralization, chamber and Kaufman gun pressures, N_2 flow rate, substrate configuration) were used. We have determined parameters that have increased the amount of $N@C_{60}$ produced per bombardment run. However, the ratio of $N@C_{60}$ to C_{60} appears invariant. ESR measurements have confirmed the narrow 3 line hyperfine split spectra of N^{14} in $N@C_{60}$ and its concentration has been determined. Progress has been made setting up a HPLC chromatographic process for separating $N@C_{60}$ from C_{60}. The first HPLC run showed a dramatic elimination of the impurity ESR signal relative to the $N@C_{60}$ signal. We have also attempted to use the N ion charging scheme on open-cage fullerenes, possessing an eight-member-ring orifice. We have yet to demonstrate using ESR that N is contained in a high symmetry environment in the open cage structures.

We have used the electron beam lithography facility in the Center for Nanoscale Materials to make both Au- C_{60} – Au and Ni-C_{60}-Ni tunnel junctions. Using shadow masks and off-normal vapor deposition of Au or Ni, we have made very fine junctions that can be easily broken by electro-migration at about 1 volt in order to form ~1nm break junctions that serve as tunnel junctions to the $C_{60.}$ These junctions demonstrate staircase I-V curves indicative of single electron tunneling at room temperature.

Program Impact:
The Quantum Computation with Electron Spins program started in July 2005 and program impacts are expected in the future.

Interactions:
Our collaborations extend within 5 groups in MSD and within CNM, BIO, CHM and Northwestern University.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Personnel Commitments for FY2005 to Nearest +/- 10%:
F. Fradin (25%), J. Schlueter (10%), C. Liu-postdoctoral appointee (25%), P. Messina-postdoctoral appointee (10%).

Authorized Budget (BA) for FY03, FY04, FY05:
FY03: **BA** $0K **FY04:** BA $0K **FY05**: BA $400K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020301

FWP and/or subtask Title under FWP:
Nanostructured Thin Films

FWP Number: 57504

Program Scope:
The Nanostructured Thin Films Program is an integrated effort involving synthesis, characterization, and computer simulation. Research within the program has focused on the fundamental science related to the synthesis of nanostructured carbon materials, especially the development of novel plasma and growth chemistries and also quantum chemical computational studies of growth processes and electronic structure. The program also exhibits a high degree of world leadership in advancing the characterization of these materials using a variety of techniques including state-of-the-art electron microscopies and synchrotron-based techniques, and in so doing leverages many of the unique resource available only at ANL. Work is also focused on the mechanical, tribological, electrochemical, and transport properties of nanocrystalline diamond films either at ANL or via collaborations with leading researchers at other national labs, and universities. The program also supports a computational methods development effort that is used in these programs as well as others, and is recognized worldwide.

Major Program Achievements (over duration of support):
Hybrid nanocarbon thin films consisting of nanocrystalline diamond and carbon nanotubes have been simultaneously synthesized. This work provides a new synthesis pathway for the synthesis of materials that combine different allotropes of carbon at the nanoscale. The surface energy of UNCD has been demonstrated using AFM-based nanoasperity measurements to be extremely low and stable even after exposure to air. Low-stiction diamond structural layers in MEMS could function in air without the need for anti-stiction coatings or hermetic sealing. Monolithic UNCD AFM probes have been successfully fabricated and used to image hard surfaces without a loss in resolution due to tip wear and have also been successfully used for dip-pin lithographic patterning of biomolecules. The competing growth and nucleation processes involved in the formation of UNCD films have been investigated using extensive quantum chemical simulations and have been used to explain the dependence of the morphology of the films on temperature. Quantum chemical techniques have given insight into the chemical bonding at the interface in diamond- carbon nanotube composites. The methods development has resulted in new advances in accuracy quantum chemical techniques.

Program Impact:
This program is widely recognized as the leading program in the world on nanostructured carbon materials. The work has lead to numerous invited talks and publications including articles in Nature-Materials, Advanced Materials, Langmuir, Physical Review Letters, and several in Applied Physics Letters. The program organized and hosted a major international diamond conference (The 8th Applied Diamond Conference/NanoCarbon 2005) at ANL in May 2005.

Interactions:
This program has extensive collaborative relationships within the Materials Science Division, Argonne National Laboratory, and throughout the world. We also make substantial use of major user facilities at ANL such as the Advanced Photon Source, the Electron Microscopy Center, the Laboratory Computing Center, and elsewhere at the Advanced Light Source (Berkeley, CA), the Materials Research Laboratory (UIUC), and Synchrotron Radiation Center (Stoughton, WI).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
2003 R&D 100 Award, ISI Highly Cited Researcher in Chemistry, 1980-1999 (Larry Curtiss), 2000 MRS Medal (Dieter Gruen)

Personnel Commitments for FY2005 to Nearest +/- 10%:
J. A. Carlisle (50%), L. A. Curtiss (50%), D. M. Gruen (50%)

Authorized Budget (BA) for FY03, FY04, FY05:
FY03 BA $860K **FY04 BA $**1,034K **FY05 BA $**924K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Nanostructured Biocomposite Materials for Energy Transduction

FWP Number: 57525

Program Scope:
This program involves the synthesis and characterization of nano- or meso-structured materials that either mimic or exploit biomolecules to store and transduce energy. The program involves three integrated tasks focused on developing biomolecular materials for energy transduction. Specifically, these include the synthesis of biomimetic soft materials (complex fluids, ionogels) for organizing a variety of biomolecules (e.g., soluble and membrane proteins) or nanoparticles (semiconductors or metals), synthesis of hard materials (rigid mesoporous inorganic frameworks, ferroelectric thin films, carbon nanostructures) tailored for enhanced electronic transport or photon-induced processes and the integration of these soft and hard materials to from robust, functional biocomposites.

Major Program Achievements (over duration of support):
Developed three families of thermoresponsive soft nanostructures whose supramolecular architecture and physical properties can be altered by modest changes in temperature. Demonstrated the utility of these materials in controlling the collective properties of encapsulated guests (host-mediated energy transduction).

Developed ionic-liquid –based gels whose structure can be tuned by controlled addition of water. Demonstrated that these ionogels can serve as templates, directing the particle morphologies of nanoparticles photochemically synthesized within them to yield previously unattainable particle shapes and thus, novel optical properties.

Successfully applied combinatorial phage display methods to identify a circularly constrained heptapeptide sequence that strongly associates with perovskite ferroelectrics that can now be used to selectively pattern ferroelectric thin films and couple and actuate tethered biomolecules.

Program Impact:
Hybrid soft-hard materials that can stabilize active biomolecules have been synthesized, thereby laying the groundwork for the assembly of functional, protein-based materials.

Interactions:
Internal: Condensed Matter Physics and Materials Engineering Physics sections of MSD, CNM, APS, Biosciences.
External: Northwestern University, University of Puerto Rico, University of Chicago, University of Wisconsin-Madison

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
25 Invited talks since 2002 (program start) – M. Firestone
Invited Member of International Institute of Nanotechnology – Northwestern University – M. Firestone
James Flack Norris Award for Physical-Organic Chemistry, Professor Michael R. Wasielewski

Personnel Commitments for FY2005 to Nearest +/- 10%:
M. A. Firestone (60%), P. Zapol (20%), J. Carlisle (10%), L. E. Iton (100%, STA), P. Laible (30%), N. Grynaviski (50%, Post-doc), D. Hay (100%, Post-doc), J. Wang (100%, Post-doc), C. Burns (50%, Post-doc), M. R. Wasielewski (subcontract to Northwestern University).

Authorized Budget (BA) for FY03, FY04, FY05:
FY03: BA \$601K **FY04: BA** \$731K **FY05: BA** \$675K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Molecular Materials

FWP Number: 58510 (including FWP 57502 thru Sept. 2004)

Program Scope:
World-class fundamental research on materials with the aim to develop new chemistry for synthesizing molecular and nanoscale building blocks to create macroscopic materials that have unique architectures, and ultimately to create new materials that have novel functional properties. The program successfully integrates expertise in synthesis, physical characterization, and computer simulations to address some of the most challenging problems in materials chemistry. The research encompasses two related thrusts. The first is the tailoring of molecular framework architectures through supramolecular chemistry. The second involves the control of size, shape, and functionality of nanoscale building blocks such as nanoparticles, nanowires, and nanotubes and the integration of these units into materials with desired properties. In addition, a computational component provides theoretical insight into various aspects.

Major Program Achievements (over duration of support):
(1) A new type of framework material for catalysis based on a nanoporous membrane that uses an electrochemical procedure to make a porous alumina and then functionality is built into the pore surface by atomic layer deposition.
(2) Cationic templation has been used to explore a new class of framework materials based on anionic dicyanamide complexes. This work has revealed the first examples of triangular, triple ladder and lithium strontinate lattice types, the first examples of long range antiferromagnetic and spin canted magnetic ordering as well as the first copper and chromium based salts. (3) Development of electrochemical techniques to make anodized aluminum oxide (AAO) with ordered arrays with controlled geometries. (4) Use of AAO as a template to make nanowires, nanotubes, antidot arrays with novel properties such as a new type of Pd nanotube that has higher sensitivity and response time to hydrogen than conventional Pd thin film sensors. (5) Studies of gold nanocrystals have revealed controlling factors of synthesis and assembly. Experiments on Co and FePt nanocrystals have demonstrated that both the ligand type and the concentration of ligand affect the formation of particles, resulting in different sizes and shapes. (6) In the first experiment of its kind to explore the dynamics of nanocrystal monolayer self-assembling process, we have found that nanocrystals with hydrophobic ligands assemble at the organic solvent-air interface rather than at the solvent/substrate interface. (7) A new thermodynamic model based on first principles calculations has been developed that can accurately describe the morphology of an arbitrary isolated nanoparticle as a function of size, shape, temperature, and chemical environment. It has been applied to explain melting of gold nanoparticles.

Program Impact:
The synthesis effort is leading to new and exciting nanostructured materials with potential for applications in sensors, catalysis, photonics and advanced electronic and magnetic materials. Our unique capabilities in the design, synthesis, and characterization of new materials have led to close interaction with other groups in the Materials Science Division, as well as the worldwide scientific community. We have also been closely involved with the development of new lab-wide initiatives on hydrogen, catalysis, solar energy, and biomaterials as well as the Center for Nanoscale Materials.

Interactions:
Internal— Collaborations with Superconductivity and Magnetism, Magnetic Films, Synchrotron Radiation and Surface Chemistry Groups. Participation in new initiatives on Biomaterials, Hydrogen, Catalysis, and Solar. Collaborations with other Argonne divisions including the Center for Nanoscale Materials, Chemistry, Advanced Photon Source, Intense Pulse Neutron Source, Energy Technology, and Math and Computer Sciences.
External— Over 50 collaborations with national and international research facilities, such as the University of Chicago, Northwestern University, University of Illinois-Chicago, Indiana University, etc.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Over 100 publications in the past three years, numerous invited review articles, one review book, over 30 invited talks. Organized symposia and workshops. Journal covers have featured our research. Numerous citations to papers, including one group member named a Highly Cited Researcher in Chemistry by ISI for the period 1981-1999 (Curtiss). Organic superconductor research was named one of the 100 top scientific discoveries funded by the DOE Office of Science.

Personnel Commitments for FY2004 to Nearest +/- 10%:
H. Wang (80%), J. Schlueter (80%), U. Geiser (80%), M. Firestone (30%), X-M. Lin (10%), L. Curtiss (10%), P. Zapol (10%)

Authorized Budget (BA) for FY03, FY04, FY05:
FWP 57502 **FY03: BA** \$200K **FY04:** combined with FWP 58510
FWP 58510 **FY03: BA** \$850K **FY04: BA** \$1,024K **FY05:** \$1,150K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020301

FWP and/or subtask Title under FWP:
Directed Energy Interaction with Surfaces

FWP Number: 58600

Program Scope:
The interaction of directed energy sources such as energetic ions, electrons, and photons with surfaces provides the basis for modifying, patterning and analyzing surfaces. This program investigates the fundamentals of these complex interactions over a wide range of conditions using several unique, world-class methods developed in our laboratory. These uniquely sensitive tools for trace analysis are also providing, for the first time, mass based analysis of materials with nanometer scale lengths.

Major Program Achievements (over duration of support):
We have built and demonstrated the world's most sensitive trace analysis mass spectrometer. The high useful yield (>30%) of this device opens the possibility for mass based analysis of nano-materials and the unique discrimination allows measurements in the ppt range. In this period high lateral (50 nm) and depth (1 monolayer) resolution has been added to make this instrument an imaging nanoprobe.

While mass spectrometry is a powerful method for analyzing surface bound species and for molecular imaging of tissue, it frequently suffers from difficulties in forming ions that are structurally and quantitatively representative of complex organic surface species, especially for multicomponent surfaces. A versatile strategy has been demonstrated at ANL to address these shortcomings: threshold single photon ionization (SPI) of desorbed neutral molecules that proceeds by localized ionization of a chemical tag bound to a molecular analyte. In this period, a range of tags have been developed for addition in both aqueous and non-aqueous environments.

Sputtering of molecules from alloys has been explored to understand the details of sputtering. This work demonstrates the ability (and its limits) of mass spectrometry to function as a local structural tool.

Program Impact:
Directed Energy sources represent an important method for analyzing, patterning and modifying nano-materials. The instruments and fundamental studies here quantify the limits of these techniques for nano-material development. The trace analysis capability leads the world for trace analysis at nanoscale dimensions.

Interactions:
Collaborative publications with a wide range of University (including University of Chicago, Washington University St. Louis, California Institute of Technology, University of Newcastle) and National Labs (ANL, SNL, and LLNL) have appeared in the last few years. Further, our unique tools are applied in collaborative research on problems of particular importance to DOE. This work includes studies of optical damage with the National Ignition Facility and studies of surface oxidation and corrosion with both SCLTR and the Office of Industrial Technologies' Aluminum Vision.

Recognitions, Honors and Awards (at least in some part attributable to support under this FWP or subtask):
2001 Energy 100 Award (One of the best 100 scientific accomplishments of the 20th Century; DOE-BES)

Personnel Commitments for FY2005 to Nearest +/- 10%:
M. J. Pellin (25%), W. F. Calaway (80%), M. R. Savina (15%), Igor Veryovkin (15%)

Authorized Budget (BA) for FY03, FY04, FY05:
FY03: BA $550K **FY04: BA** $530K **FY05: BA** $520K

Laboratory Name: Argonne National Laboratory
B&R Code: KC20301

FWP and possible subtask under FWP:
Fundamental Studies of Electrocatalysis for Low Temperature Fuel Cell Cathodes

FWP Number: 58601 (funded in FY05)

Program Scope:
This program focuses on fundamental, molecular-level study of the oxygen-reduction reaction occurring on the surfaces of electrocatalysts for the fuel cell cathode. The structures, chemical states of reactants, products, and reaction intermediates formed on these electrocatalysts are studied in addition to the kinetic parameters of the reaction. The most advanced x-ray techniques available at the Advanced Photon Source, complemented by electrochemical techniques, scanning probe microscopy, and theoretical modeling, are used. We investigate the whole system, namely, the mono- or sub-monolayer sensitive molecular orientation and short- and long-range structures of oxygen molecules, reaction intermediates, poisons, spectators, and the chemical states and core-binding energy shift of surface atoms on electrocatalyst itself. The electrocatalysts include model catalysts and realistic catalysts of platinum and platinum alloys. We investigate in-situ electrocatalytic systems with varying degrees of complexity, ranging from single crystals, to designed nano-arrays, to real fuel cell catalysts, and to single nanoparticles. The basic knowledge obtained from this study can be used to guide the development of future electrocatalysts.

Major Program Achievements (over duration of support):
This is a new program awarded in June 2005.
Our main accomplishments so far are fabrication of new model catalysts.
Novel model catalysts, one-dimensional (111)-(100) nanofaceted platinum surfaces, were fabricated.
Two-dimensional array model catalysts of Pt and Pt alloys are being fabricated.
New cooperative crossover mechanism in oxygen-reduction catalytic activities is being investigated based on significantly higher activities than expected from single crystal surfaces.

Program Impact:
A new concept of cooperative crossover reaction mechanism is being developed. The new mechanism will guide design of new real catalysts and model catalysts. Heterogeneous, alloyed catalysts will be fabricated and tested.

Interactions:
Internal --- Advanced Photon Source, Center for Nanoscale Materials, Chemical Engineering Division.
External --- U. of Illinois at Urbana, Lawrence Berkeley Laboratory, U. of Minnesota, Kent State U.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
HY: Coorganizer of “Workshop on Catalysis Research at Advanced Photon Source”, Sep. 13-14, 2005. Invited talks at Electrocatalysis symposiums of Electrochemical Society and Pacifichem-2005 meetings.
DM: Invited Talk, Fuel Cells Durability Conference, Washington, D.C., December 8-9, 2005.
YT: Farris Family Innovation Fund award and Research and Creativity award, Kent State U.

Personnel Commitments for FY2005 to Nearest +/- 10%:
H. You (30%), N.M. Markovic (10%), D. Myers (10%), G. Karapetrov (10%), P. Zapol (10%), 4 Postdocs

Authorized Budget (BA) for FY03, FY04, FY05:
FY03 BA $ 0 **FY04 BA $ 0** **FY05 BA $760K**